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(54) IMPROVEMENTS IN OR RELATING TO THIN FILM DEPOSITION

(71) We, BARR AND STROUD LIMITED, a British Company, of Anniesland, Glasgow, W.3, Great Britain, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of and apparatus for depositing a thin film on a surface by evaporation within a vacuum chamber.

In a known method the surface is subjected to ionic bombardment in a glow discharge at a pressure of approximately 10^{-2} torr within the vacuum chamber prior to the deposition of the thin film, whereby the surface is cleaned to enable good adhesion of the thin film.

In order to obtain optimum quality of deposited thin film the deposition requires to take place at a pressure of approximately 10^{-5} torr and at this pressure the glow discharge cannot be maintained. In fact, the glow discharge cannot be sustained below about 10^{-3} torr due to an insufficiency of ions and there is therefore a considerable time delay from the time the discharge is extinguished until the deposition pressure is reached. This time delay depends upon the size of the vacuum chamber and upon the pump used but is not usually less than about five minutes during which time the surface can become substantially recontaminated by adsorption of gas. From theoretical considerations it can be shown that at a pressure of 10^{-5} torr a monolayer of gas is adsorbed onto a surface in approximately one fifth of a second.

It is an object of the present invention to obviate or mitigate the above disadvantage.

According to the present invention there is provided a method of depositing a thin film on a surface by evaporation within a vacuum chamber which includes a discharge source of electromagnetic energy for effecting cleaning of a said surface, said method including the steps of reducing the pressure within the chamber to approximately 10^{-5} torr, energising said source of energy, leaking gas into the chamber to raise the pressure therein to approximately 5×10^{-5} torr to enable discharge from said source to be sustained, during said discharge heating the evaporant and confining heated evaporant in an enclosure, and releasing said heated evaporant after a predetermined time whereby the evaporant is deposited in thin film form on the surface.

Preferably, simultaneously or substantially simultaneously with the heated evaporant being released, the source of energy is de-energised and the leakage of gas into the chamber is terminated.

Preferably also the energy emitted by said source is in the ratio frequency waveband.

Also, according to the present invention there is provided apparatus for carrying out the method according to the present invention, said apparatus including a vacuum chamber, an enclosure for an evaporant in said chamber, means for heating an evaporant when located in said enclosure, a holder in said chamber, for a surface whereon said evaporant is to be deposited, a valve for leaking gas into said chamber, and a discharge source of electromagnetic energy having a quarter-wavelength aerial.

Where more than one thin film is to be deposited the method according to the present invention may be employed as instanced in the following paragraphs:

(a) First and second thin films may be successively deposited on a surface by the steps of reducing the pressure within the chamber to approximately 10^{-5} torr, energising said source of energy, leaking gas into the chamber to raise the pressure therein to approximately 5×10^{-5} torr to enable a discharge from said source to be sustained, during said discharge heating each of said evaporants and separately confining each heated evaporant in an enclosure, and, after a predetermined time releasing the first heated evaporant, and after a predetermined interval of time releasing

the second evaporant whereby the evaporants are successively deposited in thin film on the surface during the discharge alternatively

(b) first and second thin films may be successively deposited on a surface by the steps of reducing the pressure within the chamber to approximately 10^{-5} torr, energising said source of energy, leaking gas into the chamber to raise the pressure therein to approximately 5×10^{-5} torr to enable a first discharge from said source to be sustained, during said first discharge heating at least the first of said evaporants and separately confining each heated evaporant in an enclosure, and after a first predetermined time, simultaneously or substantially simultaneously releasing the first of said heated evaporants, de-energising said source of enerby, and terminating said leakage of gas into the chamber, whereby the first evaporant is deposited in thin film form on the surface, after a second predetermined time energising said source of energy, confining said first evaporant in its enclosure, leaking gas into the chamber to raise the pressure therein to approximately 5×10^{-5} torr to enable a second discharge from said source to be sustained, during said second discharge heating the second of said evaporants and confining the heated evaporant in its encolsure, and after a third predetermined time simultaneously releasing the second heated evaporant, de-energising said source of energy and terminating said leakage of gas into the chamber, whereby the second evaporant is deposited in thin film in succession to said first evaporant on said surface;

(c) during the method of successively depositing the first and second thin films on a surface according to paragraph (b) above said first evaporant may be confined to its enclosure simultaneously or substantially simultaneously with the sustaining of said second discharge; alternatively

(d) first and second thin films may be successively deposited on a surface by the steps of reducing the pressure within the chamber to approximately 10^{-5} torr, energising said source of energy, leaking gas into the chamber to raise the pressure therein to approximately 5×10^{-5} torr to enable a first discharge from said source to be sustained, during said first discharge heating at least the first of said evaporants and separately confining each heated evaporant in an enclosure, and after a first predetermined time, simultaneously or substantially simultaneously releasing the first of said heated evaporants, de-energising said source of energy, and terminating said leakage of gas into the chamber, whereby the first evaporant is deposited in thin film form on the surface, after a second predetermined time energising said source of energy, confining said first evaporant in its enclosure, leaking gas into the chamber to raise the pressure therein to approximately 5×10^{-5} torr to enable a second discharge from said source to be sustained, during said second discharge heating the second of said evaporants and confining the heated evaporant in its enclosure, and, after a third predetermined time releasing the second heated evaporant whereby the second evaporant is deposited in thin film form in succession to said first evaporant, on the surface during the discharge; alternatively

(e) first and second thin films may be successively deposited on a surface by the steps of reducing the pressure within the chamber to approximately 10^{-5} torr, energising said source of energy, leaking gas into the chamber to raise the pressure therein to approximately 5×10^{-5} torr to enable a discharge from said source to be sustained, during said discharge heating at least the first of said evaporants and separately confining each heated evaporant in an enclosure, and, after a first predetermined time releasing the first heated evaporant whereby the first evaporant is deposited in thin film form on the surface during the discharge, after a second predetertimed time confining said first evaporant in its enclosure, heating the second of said evaporants, and, after a third predetermined time simultaneously releasing the second heated evaporant, de-energising said source of energy and terminating said leakage of gas into the chamber, whereby the second evaporant is deposited in thin film form in succession to said first evaporant on said surface; alternatively

(f) first and second thin films may be successively deposited on a surface by evaporation within a vacuum chamber which includes a discharge source of electromagnetic energy for effecting cleaning of a said surface by the steps of reducing the pressure within the chamber to approximately 10^{-5} torr, energising said source of energy leaking gas into the chamber to raise the pressure therein to approximately 5×10^{-5} torr to enable a discharge from said source to be sustained, heating at least the first evaporant and separately confining each heated evaporant in an enclosure, and, after a predetermined time simultaneously or substantially simultaneously releasing the first heated evaporant, de-energising said source and terminating the leakage of gas into the chamber and heating the second evaporant and confining the second heated evaporant in its enclosure, whereby the first evaporant is deposited in thin film form on the surface, after a further interval of time confining said first heated evaporant to its enclosure and simultaneously or substantially simultaneously releasing the second heated evaporant whereby the second evaporant is deposited in thin film form in succession to the first evaporant on the surface;

(g) during the method of successively depositing first and second thin films on a sur-

face according to paragraph (d) above said first evaporant may be confined to its enclosure simultaneously or substantially simultaneously with the sustaining of said second discharge;

(h) a plurality of thin films may be successively deposited on a surface by depositing the first and second thin films according to the method of paragraphs (b), (c), or (e) above and depositing at least one of the remaining thin films in a manner similar to that of the second thin film, the other remaining thin films, if any, being deposited in a manner similar to that of the second thin film in the method according to either of paragraphs (d) or (f) above; alternatively

(i) a plurality of thin films may be successively deposited on a surface, the first and second thin films being deposited according to the method of either paragraphs (a) or (d) above and at least one of the remaining thin films being deposited in a manner similar to that of the second thin film in the method according to either of paragraphs (b) or (f) above, the other remaining thin films, if any, being deposited in a manner similar to that of the second thin film; alternatively

(j) a plurality of thin films may be successively deposited on a surface, the first and second thin films being deposited according to the method of any one of paragraphs (b), (c) or (e) above, and at least one of the remaining thin films being deposited in a manner similar to that of the second thin film in the method according to either of paragraphs (d) or (f) above, the other remaining thin films, if any, being deposited in a manner similar to that of the second thin film; alternatively

(k) a plurality of thin films may be successively deposited on a surface, the first and second thin films being deposited according to the method of paragraph (f) above, and at least one of the remaining films being deposited in a manner similar to that of the second thin film in the method according to any one of paragraphs (a), (b), or (f) above, the other remaining thin films, if any, being deposited in a manner similar to the second thin film.

An embodiment of the apparatus according to the present invention will now be described, by way of example, with reference to the drawings accompanying the provisional specification, in which:

Fig. 1 shows a glass vacuum chamber according to the present invention; and

Fig. 2 shows a metal vacuum chamber according to the present invention.

In Fig. 1 the apparatus includes a glass vacuum chamber 10, having a needle valve 9 in the wall thereof, which chamber is sealingly seated on a base 11. A holder 12 for a substrate 13 on the surface of which a thin film is to be deposited is supported on the base 11 within the chamber 10. The base 11 also supports an enclosure 14 for an evaporant and the enclosure 14 includes means for heating evaporant within the enclosure and a pivotally-mounted shutter 15 which is movable so as to permit heated evaporant in the enclosure 14 to be released and be deposited upon the surface of the substrate 13 and upon all other objects within its field of view.

The apparatus includes a discharge source of electromagnetic energy 16 having a radio-frequency generator 17, an amplifier 18, a transmission line 19 and a quarter-wavelength aerial 20 wound round the outside of the chamber 10.

Fig. 2 shows a modification wherein like elements have been given like numbers. In this case the chamber 10 is metal and the aerial 20 is wound on a former (not shown) and located inside the chamber 10. Two d.c.-operated coils are mounted externally of the chamber and, when energised, provide a magnetic bottle to constrain energy emitted from the aerial 20 from being discharged via the metallic walls of the chamber 10. If desired, the two d.c. operated coils may be utilised in the Fig. 1 embodiment.

The discharge source 16 also includes a matching unit 23 whereby the system may be tuned if so desired.

The generator 17 has an output power of approximately 200 watts and a frequency range of 10—20 MHz.

The method of depositing a thin film on the surface of the substrate by evaporation comprises the steps of reducing the pressure within the chamber 10 to approximately 10^{-5} torr by a pump (not shown), energising the discharge source 16, partially opening the valve 9 to admit air into the chamber 10 to raise the pressure therein to approximately 5×10^{-3} torr thereby enabling an r.f. discharge from the source 16 to strike and be sustained, during the discharge, heating the enclosure 14 containing the evaporant and confining the heated evaporant to the enclosure 14 by means of the shutter 15, and releasing the heated evaporant, by pivotal movement of the shutter 15, after a predetermined time so that the evaporant may be deposited in thin film form upon the surface of the substrate 13 in the holder 12.

The pivotal movement of the shutter 15 to realese the evaporant may take place simultaneously with the source 16 being de-energised and the leakage of air into the chamber 10 being terminated by closure of the valve 9, or the evaporation may be effectetd through the r.f. discharge from the aerial 20.

A plurality of thin films may be deposited successively upon the substrate 13, in which case the r.f. discharge from the aerial 20 may be continuous and each film deposited in succession from each of a plurality of enclosures 14 having shutters 15, through the discharge, or evaporation of successive thin films

may occur between periods of r.f. discharge from the source 16, in which case there is substantially no time-lag between the steps of evaporating and the r.f. discharge. Alternatively, the r.f. discharge may take place before deposition of the first thin film only.

In one example of the method of thin film deposition according to the present invention using the apparatus shown in Fig. 1, a glass substrate was mounted in the holder 12 and a quantity of magensium fluoride placed in the enclosure 14. The pressure within the chamber was 10 thereafter reduced by a pump (not shown) to approximately 10^{-5} torr, and the discharge source 16, set to operate at 14.3 MHz and 200 watts, energised. At this low pressure no discharge was sustained therefore the valve 9 was partly opened to permit entry of air into the chamber 10 until such time as the discharge was sustained, which occurred at a pressure of approximately 5×10^{-5} torr. The discharge was maintained for a period of 12 minutes to render the surface of the substrate atomically clean during which time the magnesium fluoride evaporant was heated for approximately 3 minutes to a temperature of approximately 1400°C and thereafter the needle valve 9 was closed and the source 16 was de-energised causing the discharge to be extinguished which, in turn, suddenly reduced the pressure within the chamber to approximately 5×10^{-6} torr; simultaneously evaporation and deposition occurred by removal of the shutter 15. The film thickness was directly proportional to the deposition time, and a film having an optical thickness of 140 nanometres was deposited in 60 seconds.

On completion of the evaporation process the evaporant was allowed to cool for about five minutes after which time air was admitted to the chamber 10 through the valve 9 thereby enabling the pressure within the chamber to build up to atmospheric pressure in about one minute.

The coated glass substrate produced as a result of this process exhibited anti-reflection properties in the visible spectrum.

The period of 12 minutes for pre-deposition cleaning by the r.f. discharge was determined by conducting a number of runs of magnesium fluoride coatings on glass substrates, with differing amounts of r.f. pre-treatment, and then conducting a durability test on each coated substrate. The r.f. pre-treatment time for maximum durability was found to be 12 minutes.

A known previous method of obtaining a durable anti-reflection coating on a glass substrate required the substrate to be maintained at a temperature of 300°C during the deposition. This known method however, involves slow heating and cooling respectively before and after deposition in order to avoid the introduction of thermal stresses so that the process from start to finish usually takes three or more hours.

The coated glass substrate obtained as a result of the method described in example one above was subjected to the abrasion test described in FVRDE Specification 2024, and the results compared with those of a sample prepared by the above-mentioned known heated-substrate method.

The results showed the sample obtained in example one to have a SIRA (British Scientific Instruments Research Association) grading of 0—1 whereas the conventionally-obtained sample has a SIRA grading of 2. As is well known, the SIRA gradings are:

0 — unaffected
1 — slightly scratched
2 — moderately scratched
3 — heavily scratched
4 — clear streaks
5 — film completely removed

It will be appreciated that in addition to the improved durability the cycle time for production of the anti-reflection coating is reduced from approximately three hours to less than one hour.

In a second example aluminium was deposited on a glass substrate which had previously been cleaned in the apparatus shown in Fig. 1 by a discharge from the source 16 set to operate at 14.3 MHz and 200 watts. The discharge was maintained for a period of 12 minutes to render the surface of the substrate atomically clean during which time the aluminium evaporant was heated for 1 minute to a temperature of 1180°C in the shutter-covered holder 14 in order to de-gas the evaporant. Immediately on de-energisation of the source 16 the pressure fell to approximately 5×10^{-6} torr and the shutter 15 was removed substantially simultaneously for a period of 30 seconds at the end of which time the substrate was covered with an opaque film of aluminium. Thereafter the evaporant was allowed to cool for about 5 minutes, and air was then admitted to the chamber 10 through the valve 9 and the pressure within the chamber reached atmospheric pressure in about 1 minute.

Hitherto the preparation of anti-reflection coatings on the surface of substrates transmitting radiation in the infra-red wavelength band has been restricted by the poor mechanical properties of the coatings due mainly to the soft nature of the substrates and the thickness of the films required. Suitable substrates are silicon, germanium, arsenic triselenide, and arsenic trisululphide and the use of r.f. cleaning prior to deposition of the coating has led to greatly improved adhesion and stability, as is instanced in the comparison of time taken for crazing to occur by immersion in water of samples prepared by a conventional method and by the method according to the present invention:

	Time for crazing to commence	
	Conventional Sample	r.f. pre-treated sample
Arsenic trisulphide	45 seconds	65 hours
Germanium	Less than five seconds	4 hours

In an example of the preparation of two layer anti-reflection coatings on the surface of substrates of arsenic triselenide and arsenic trisulphide it was found that the stress produced at the interface between the substrate and the first deposited layer was much greater than that produced between the first and second layers and the r.f. pre-treatment of the present invention was applied prior to deposition of the first layer with a view to mitigating the stress at the interface between the substrate and first layer.

In the case of the arsenic triselenide substrate it was found to be impossible to complete the deposition of the first layer using the known method before disintegration occurred, unless the r.f. discharge pre-treatment of the present invention was used.

In the case of the arsenic trisulphide substrate it was found that the deposited coating (two layers) disintegrated several minutes after exposure to air, unless the r.f. discharge pre-treatment of the present invention was used.

Consequently, in these two cases no comparison for durability can be made to assess fully the effect of the r.f. discharge pre-treatment. However, the following test results were achieved on the r.f. pre-treatment films deposited in accordance with the invention:

Test	Arsenic triselenide substrate	Arsenic trisulphide substrate
Water immersion at room temp: Time for crazing to commence	168 hours	65 hours
Abrasion test: Pellet of SIRA rubber No. 2 loaded with 250 gm. and placed in abrasive wear resistance device. Each sample rubbed 150 strokes and percentage area of coating completely removed was measured	0%	0.4%
Adhesive tape test: A piece of adhesive tape pressed firmly onto coating then slowly pulled off. The effect was noted	Coating unaffected	Coating unaffected
Rouge test: A felt pad impregnated with rouge and methyl alcohol rubbed on coating to remove coating	Coating partly removed with difficulty	Coating partly removed with difficulty

In a further example aluminium was deposited by the method of the invention upon the surface of a glass substrate during the r.f. discharge. In this case the hardness of the coating was found to be comparable to that of a silicon monoxide-overcoated aluminium film deposited by a conventional method.

WHAT WE CLAIM IS:

1. A method of depositing a thin film on a surface by evaporation within a vacuum chamber which includes a discharge source of electromagnetic energy for effecting cleaning of a said surface, said method including the steps of reducing the pressure within the chamber to approximately 10^{-5} torr, energising said source of energy, leaking gas into the chamber to raise the pressure therein to approximately 5×10^{-5} torr to enable a discharge from said source to be sustained, during said discharge heating the evaporant and confinining heated evaporant in an enclosure, and

releasing said heated evaporant after a predetermined time whereby the evaporant is deposited in thin film form on the surface.

2. The method according to claim 1, wherein simultaneously or substantially simultaneously with the heated evaporant being released the source of energy is de-energised and the leakage of gas into the chamber is terminated.

3. The method according to either preceding claim, wherein the energy emitted by said source is in the radio-frequency waveband.

4. The method according to claim 3, wherein the energy emitted is in the frequency range 10—20 MHz.

5. A method of depositing a thin film on a surface substantially as hereinbefore described with reference to the accompanying drawings.

6. Apparatus for carrying out the method according to any preceding claim, said apparatus including a vacuum chamber, an enclosure for an evaporant in said chamber, means for heating an evaporant when located in said enclosure, a holder for a substrate in said chamber, a valve for leaking gas into said chamber, and a discharge source of electromagnetic energy having a quarter-wavelength aerial.

7. Apparatus according to claim 6, wherein said aerial is mounted on the chamber which is made of a non-conductive material.

8. Apparatus according to either of claims 6 or 7, wherein said chamber is made of glass.

9. Apparatus according to claim 6, wherein said chamber is made of metal and the aerial is located inside the chamber.

10. Apparatus according to any one of claims 6—9, including means for creating a magnetic bottle to contain electromagnetic energy released from said source.

11. Apparatus according to any one of claims 6—10, wherein said discharge source includes a radio-frequency generator and a transmission line connected between the generator and the aerial.

12. Apparatus for carrying out the method according to any one of claims 1—5, substantially as hereinbefore described with reference to Fig. 1 of the drawings accompanying the provisional specification.

13. Apparatus for carrying out the method according to any one of claims 1—5, substantially as hereinbefore described with reference to Fig. 2 of the drawings accompanying the provisional specification.

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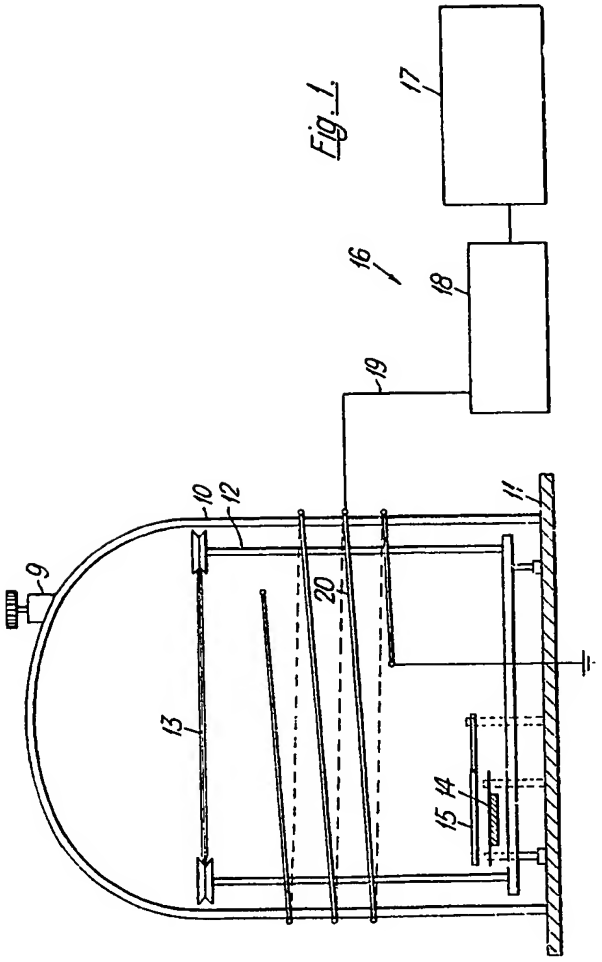
1263582 PROVISIONAL SPECIFICATION
2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*
Sheet 1

Fig. 1.



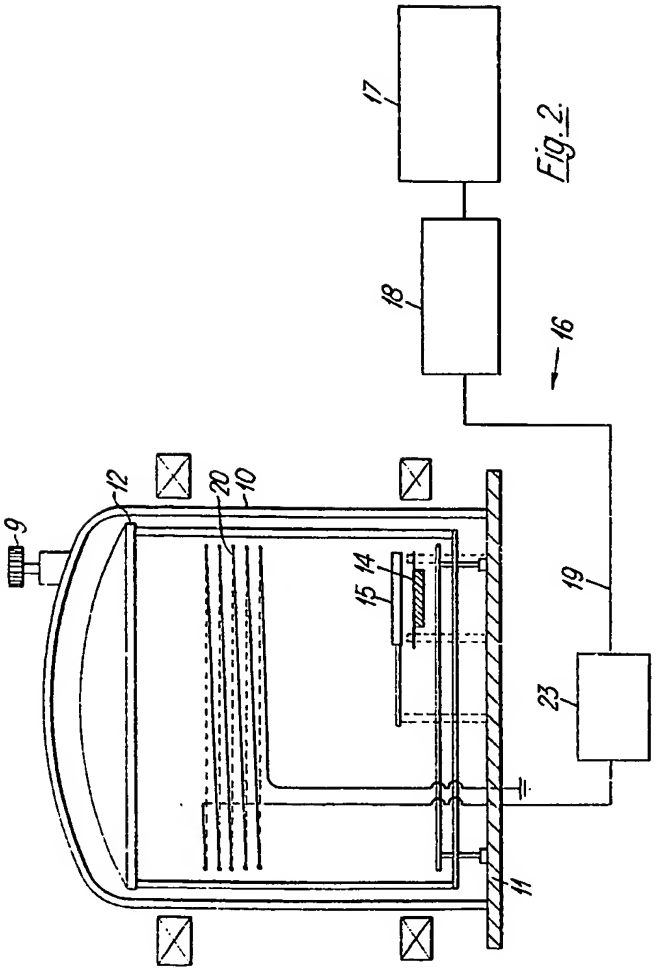


Fig.2.